

## EPODOC / EPO

PN - JP11134944 A 19990521  
PD - 1999-05-21  
PR - JP19970295986 19971028  
OPD - 1997-10-28  
TI - HIGHLY THERMALLY CONDUCTIVE INSULATING MATERIAL AND SUPERCONDUCTIVE CABLE  
IN - NAGAYA SHIGEO; ONO AKINOBU; MIYATA HIROYUKI  
PA - FUJIKURA LTD; CHUBU ELECTRIC POWER  
IC - H01B7/00 ; H01B3/30 ; H01B7/34 ; H01B12/12

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TI - Hyperthermia conductivity insulating material for superconductor cable - has filter having hyperthermia conductive property subjected to surface treatment  
PR - JP19970295986 19971028  
PN - JP11134944 A 19990521 DW 199931 H01B7/00 005pp  
PA - (CHUB ) CHUBU DENRYOKU KK  
(FUJD ) FUJIKURA LTD  
IC - H01B3/30 ; H01B7/00 ; H01B7/34 ; H01B12/12  
AB - JP11134944 NOVELTY - The material includes resin and filter having hyperthermia conductivity property. The surface treatment of filter is performed using silane coupling agent.  
- USE - For superconductor cables.  
- ADVANTAGE - Excels in heat conductivity even at low temperature. Since hyperthermia conductivity insulating material is used, the cable responds to speck, thus opposing cold brittleness.  
- (Dwg. 1/4)  
OPD - 1997-10-28  
AN - 1999-362723 [31]

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PA - FUJIKURA LTD; CHUBU ELECTRIC POWER CO INC  
TI - HIGHLY THERMALLY CONDUCTIVE INSULATING MATERIAL AND SUPERCONDUCTIVE CABLE  
AB - PROBLEM TO BE SOLVED: To provide a highly thermally conductive insulating material having high thermal conductivity at very low temperature and at the same time excellent resistance to low temperature brittleness and a superconductive cable.  
- SOLUTION: This highly thermally conductive insulating material contains resin and  $\geq 5$  volume % content of a surface treated filler having a high thermal conductivity. The surface treatment of the filler is preferably carried out using a silane coupling agent. This superconductive cable comprises such a highly thermally conductive insulating material as an insulator.  
I - H01B7/00 ; H01B3/30 ; H01B7/34 ; H01B12/12

## PATENT ABSTRACTS OF JAPAN

(11) Publication number : 11-134944

(43) Date of publication of application : 21.05.1999

(51) Int. Cl.

H01B 7/00

H01B 3/30

H01B 7/34

H01B 12/12

(21) Application number : 09-295986

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(22) Date of filing : 28.10.1997

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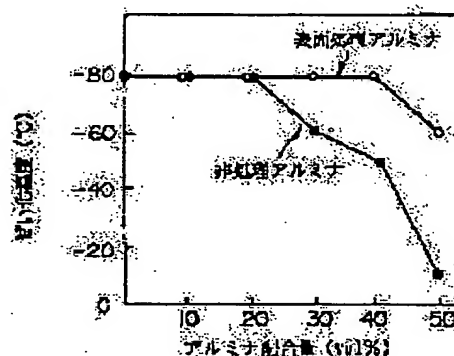
NAGAYA SHIGEO

(54) HIGHLY THERMALLY CONDUCTIVE INSULATING MATERIAL AND SUPERCONDUCTIVE CABLE

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a highly thermally conductive insulating material having high thermal conductivity at very low temperature and at the same time excellent resistance to low temperature brittleness and a superconductive cable.

SOLUTION: This highly thermally conductive insulating material contains resin and 5 volume % content of a surface treated filler having a high thermal conductivity. The surface treatment of the filler is preferably carried out using a silane coupling agent. This superconductive cable comprises such a highly thermally conductive insulating material as an insulator.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against  
examiner's decision of rejection]

[Date of extinction of right]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to the high temperature conductivity insulating material for very low temperature, and a superconductivity cable about a high temperature conductivity insulating material and a superconductivity cable.

[0002]

[Description of the Prior Art] There are some which arranged in the copper tube what twisted the superconductor on cooling pipes, such as a metallic pipe, and gave the insulator on the layer, and nothing and this layer as a superconductivity cable. And by leading a refrigerant to the refrigerant path in a metallic pipe etc., it is cooled and a superconductor is made into very low temperature. Liquid helium, liquid nitrogen, etc. are used as a refrigerant for cooling a superconductor to very low temperature.

[0003]

[Problem(s) to be Solved by the Invention] By the way, although the thermal conductivity of an insulator improved as the fill of a bulking agent increased when the constituent which filled up the resin with the inorganic bulking agent more than 5 volume % as the aforementioned insulator was used, on the other hand, there was a problem that cold brittleness became bad. Although the brittleness by general blow stress is originally seldom required of the superconductivity cable used by very low temperature, there are not few cases where the spec. of brittle temperature is set up from a viewpoint of reliability. At this time, the upper limit of the fill of an inorganic bulking agent will be restricted by brittle temperature, and was not made [ obtaining the insulator excellent in thermal conductivity and cold brittleness, or ].

[0004] While this invention was made in view of the aforementioned situation and having high thermal conductivity in very low temperature, let it be a technical problem to offer a high temperature conductivity insulating material and a superconductivity cable excellent in cold brittleness.

[0005]

[Means for Solving the Problem] Including a resin and the bulking agent which has high temperature conductivity, the content of a bulking agent which has high temperature conductivity is more than 5 volume %, and this technical problem is solved by considering as the superconductivity cable which comes to constitute an insulator using the high temperature conductivity insulating material characterized by carrying out surface treatment of the bulking agent, and this high temperature conductivity insulating material.

[0006]

[Embodiments of the Invention] In this invention, it is the bulking agent (henceforth a high temperature conductivity bulking agent) which has high temperature conductivity as a bulking agent, and that by which surface treatment is carried out is used. A high temperature conductivity bulking agent is a bulking agent of the electric insulation whose thermal conductivity is more than 0.04 cal/cm-sec and \*C in 25 degreeC, and the example is ceramics, such as metallic oxides, such as aluminum oxides, such as oxidization silicon, such as oxidization silicon, and an aluminum oxide, a boron nitride, and a beryllia. Although these inorganic bulking agents have a very-low-temperature region, for example, thermal conductivity also with 100K or less high very low temperature, unlike

bulking agents, such as a metal-powder object, they are excellent in electric insulation. If the mean particle diameter of the aforementioned bulking agent is about 1-100 micrometers, an insulating material is excellent in mechanical properties, such as tensile strength.

[0007] If a spherical alumina is used as aluminum oxides, it will be easy to fill up a resin and will be hard to wear metal mold or an extruder at the time of kneading and fabrication.

[0008] Although a boron nitride is an expensive material as compared with an aluminum oxide, since it is a soft material, it is hard to wear metal mold, an extruder, etc. at the time of kneading and fabrication. Moreover, as compared with an aluminum oxide, the insulating material excellent in thermal conductivity is given. On the other hand, an aluminum oxide will be stiff material if it compares with a boron nitride, and although it is inferior to thermal conductivity, it is cheap.

[0009] That by which surface treatment was carried out is used as a high temperature conductivity bulking agent. Surface treatment means the processing which processes the front face of a high temperature conductivity bulking agent by coupling agent, and raises adhesion with a resin. The example of coupling agent is a silane coupling agent. A silane coupling agent is a silicon atom content compound which has in a monad the adding-water resolvability machine which produces the silanol group of the property which forms the front face and chemical bond of this bulking agent by the condensation reaction with the hydroxyl group or surface attached groundwater contained in a high temperature conductivity bulking agent, and a functional group combinable with a resin.

Alkoxy groups, such as a methoxy group, are mentioned as a adding-water resolvability machine, and the amino group, a vinyl group, an epoxy group, a sulfhydryl group, a thiocyanate machine, tetrapod sulfene, etc. are mentioned as a functional group. A resin and bridge formation are possible for a desirable silane coupling agent including a carbon-carbon double bond or a sulfur atom.

[0010] The example of a silane coupling agent is the thing of sulfur atom content, such as mercapto silanes, such as epoxy silanes, such as vinyl silanes, such as vinyltrimetoxysilane, and gamma-glycidoxypropyltrimetoxysilane, or gamma-mercapto propyltrimethoxysilane, and screw (3-triethoxy silyl propyl) tetrapod sulfene.

[0011] What the silane coupling agent was mixed [ what ] at a rate of the about 0.1 to 8.0 weight section to this bulking agent 100 weight section as a high temperature conductivity bulking agent, and combined this coupling agent with the front face of a high temperature conductivity bulking agent is desirable. Under in the about 0.1 weight section, if an effect is not accepted but the 8.0 weight sections are exceeded, it will be superfluous and cost will become high too much.

[0012] Although the thermal conductivity of the insulating material containing a resin and a high temperature conductivity bulking agent is influenced of the thermal conductivity of a resin, its influence of a high temperature conductivity bulking agent is very large. Therefore, as for a resin, it is desirable to be chosen from thermal conductivity for the purpose of the ease of being filled up of a filler. If the bridge is constructed over the resin, an insulating material is excellent with cold brittleness. A peroxide, sulfur, etc. are mentioned as a cross linking agent.

[0013] As a resin, elastomers, such as ethylene-propylene rubber, EPDM rubber, and an ethylene octene copolymer, polyethylene, polypropylene, an epoxy resin, etc. are mentioned.

[0014] The resin manufactured using a metallocene catalyst as the aforementioned resin is desirable. Since the active spot of a Ziegler catalyst is uneven, as for the resin compounded using the Ziegler catalyst, molecular weight distribution and a copolymerization composition distribution tend to serve as broadcloth. On the other hand, the resin with which, as for the metallocene catalyst, it was manufactured using the metallocene catalyst since the active spot was a single site has molecular weight distribution and a sharp copolymerization composition distribution, and has few contents of a low molecular weight constituent. For this reason, if a high temperature conductivity bulking agent is included in the resin manufactured using the metallocene catalyst, even if it can include more these bulking agents and includes them, the mechanical property of an insulating material, lesion-proof nature, etc. cannot fall easily. [ many ] Moreover, since the resin manufactured using the metallocene catalyst has the outstanding mechanical strength even if density is low, a bulking agent can be included in this resin so much. In addition, the polyethylene manufactured using the metallocene catalyst can have about three 0.87 g/cm density and a brittle temperature below -76 degreeC.

[0015] The content of a high temperature conductivity bulking agent to which surface treatment was performed is five to 40 volume % preferably more than 5 volume % to the sum total volume of this

bulking agent and a resin. Thus, the insulating material of this invention which changes including a lot of high temperature conductivity bulking agents is excellent in the low temperature brittleness and thermal conductivity. Thermal conductivity [ in / very low temperature / that the content of a high temperature conductivity bulking agent is under 5 volume % ] is hard to be improved. If about 40 volume % is exceeded, elongation will fall and an insulating material will tend to become weak. If the content of a high temperature conductivity bulking agent is more than 5 volume %, an insulating material has the thermal conductivity of about 0.3 or more w/m-k in a room temperature (25degreeC), and has high thermal conductivity also in very low temperature. therefore, the business of this invention -- the high temperature conductivity insulating material is suitable especially as an insulating material for cooling a superconductor and insulating

[0016] Although the high temperature conductivity insulating material for very low temperature of this invention contains a resin and a high temperature conductivity bulking agent as an indispensable component, it may also contain further reinforcing materials, such as an antioxidant, a cross linking agent, processing aid, and carbon black, an extending agent, a pigment, etc. if needed.

[0017] It consists of high temperature conductivity insulating materials of the above [ the superconductivity cable of this invention / an insulator ]. Drawing 4 is the cross section showing the example, while this superconductivity cable has a superconductor 1 on the metal cooling pipes 3, such as a copper pipe, and having an insulator 2 on this superconductor 1, an insulator 2 is [ the content of a high temperature conductivity bulking agent ] more than 5 volume % including a resin and a high temperature conductivity bulking agent, and surface treatment of this bulking agent is carried out. If refrigerants, such as liquid helium, are led to the refrigerant path 4 in a cooling pipe 3, a superconductor 1 can be cooled from the inside. Moreover, if a superconductivity cable is arranged in a metallic conduit and a refrigerant is led to the path between an insulator 2 and a metallic conduit, a superconductor 1 can be cooled also from an outside. Since the content of this bulking agent is more than 5 volume % and surface treatment of this bulking agent is carried out including the resin and the high temperature conductivity bulking agent, an insulator 2 excels [ insulator / of the superconductivity cable of this invention / 2 ] in the cooling efficiency and the low-temperature physical properties by the refrigerant.

[0018] The superconductivity cable of the structure shown in drawing 4 can be manufactured by twisting a superconductor 1 on the outside of a cooling pipe 3, and covering the insulating material of this invention with extrusion molding etc. on a layer, and nothing and this layer. Since extrusion molding of the mixture containing a resin and a high temperature conductivity bulking agent is carried out and an insulator can be formed, manufacture and long-picture-izing of a superconductivity cable are easy.

[0019] As a superconductor, oxide system superconducting materials, such as superconductive metals, such as Nb, NbTi, Nb3Sn, and V3Ga, or Y1Ba2Cu3Ox, and 2(Bi, Pb) Sr2calcium2Cu3Ox, are mentioned.

[0020]

[Example] Hereafter, this invention is explained in detail. In the following examples of an examination, all the sections mean the weight section. As a bulking agent, the spherical alumina which carried out surface treatment (henceforth silanizing) by the silane coupling agent, the spherical alumina which has not carried out silanizing, the boron nitride which carried out silanizing, and four kinds of boron-nitride \*\*s which have not carried out silanizing were prepared. In addition, the particle size of an alumina and a boron nitride was almost the same. Moreover, the alumina which carried out silanizing, and the boron nitride which carried out silanizing carried out the amount mixture of said of the silane coupling agent of the same kind to an alumina and a boron nitride, and combined the silane coupling agent with these front faces.

[0021] As a base resin, the metallocene system elastomer (Dow-Jones CL 8001 by the Dow Chemical Co.) was prepared.

[0022] The elastomer 100 aforementioned section, the aforementioned alumina or the aforementioned boron nitride, the cross-linking-agent 3.5 section, and the antioxidant 1 section were mixed, and it considered as mixture. As the loadings of the alumina which carried out surface treatment were shown in Table 1, it was made to change in the range of the 50 to 450 section to the elastomer 100 section, and the loadings of the boron nitride which carried out surface treatment were

changed in the range of the 29 to 250 section to the elastomer 100 section, as shown in Table 2.

[0023] Subsequently, mixture was kneaded using the kneading roll, and this kneading object was pressed, the bridge was constructed, and the sheet was obtained. And the low temperature brittleness and thermal conductivity of this sheet were measured. With combination prescription, the measurement result of the low temperature brittleness was shown in Table 1 and Table 2. Moreover, the graph showed the relation between the loadings (volume %) of a boron nitride, and brittle temperature for the relation between the loadings (volume %) of an alumina, and brittle temperature to drawing 1 at drawing 2. The graph showed the relation between the loadings of bulking agents, such as an alumina and a boron nitride, and thermal conductivity to drawing 3. In addition, brittle temperature uses an embrittlement testing machine and is JIS. It measured by K7216. Thermal conductivity is the measured value in 298K, and was measured using the QTM quick thermal conductivity meter. In the column of the low temperature brittleness in Table 1, x mark in which \*\* mark which is excellent in O mark which is very excellent in O mark is a little inferior means \*\*\*\*.

[0024]

[Table 1]

		試験例									
		1	2	3	4	5	6	7	8	9	10
配 合	ベース樹脂(重量部)	100	100	100	100	100	100	100	100	100	100
	非処理アルミナ(重量部)	—	50	114	195	300	—	—	—	—	—
	処理アルミナ(重量部)	—	—	—	—	—	50	114	195	300	450
低温ぜい性		◎	◎	◎	○	△	◎	◎	◎	◎	○

[0025]

[Table 2]

		試験例									
		11	12	13	14	15	16	17	18	19	20
配 合	ベース樹脂(重量部)	100	100	100	100	100	100	100	100	100	100
	非処理窒化硼素(重量部)	—	29	65	112	170	—	—	—	—	—
	処理窒化硼素(重量部)	—	—	—	—	—	29	65	112	170	250
低温ぜい性		◎	◎	○	△	×	◎	◎	◎	○	△

[0026] When the alumina and boron nitride which carried out silanizing are used although the low temperature brittleness becomes bad as the loadings of an alumina and a boron nitride increase from Table 1 and Table 2, silanizing is not carried out, namely, it turns out that the low temperature brittleness cannot fall easily as compared with the case where a non-processing alumina and a boron nitride are used.

[0027] A bird clapper understands brittle temperature highly rapidly as the loadings of an alumina and a boron nitride will increase, if the alumina and boron nitride by which silanizing is not carried out are used from drawing 1 and drawing 2. On the other hand, when the alumina and boron nitride which carried out silanizing are used, drawing 1 and drawing 2 show that brittle temperature cannot become high easily. Moreover, the difference of brittle temperature with the case where silanizing has not been carried out to the case where silanizing is carried out is large, and a bird clapper is known, so that there are many loadings of an alumina and a boron nitride. Namely, it was so remarkable that the improvement effect of the low temperature brittleness by silanizing had many loadings of an alumina and a boron nitride. In the case of a boron nitride, the depressor effect of the brittle-temperature rise by silanizing shows up greatly. Although the adhesion of a boron nitride and a base resin is bad from the first, the adhesion to the base resin of a boron nitride improves

remarkably by silanizing, and for this reason, brittle temperature is presumed to be what cannot go up easily as shown in drawing 2.

[0028] When the boron nitride which carried out silanizing is used, drawing 3 shows that the insulating material excellent in thermal conductivity is obtained rather than the case where the alumina which carried out silanizing is used. Moreover, drawing 3 shows that the thermal conductivity of an insulating material does not fall depending on silanizing.

[0029] If the alumina which carried out silanizing, and the boron nitride which carried out silanizing are used, as shown in drawing 1 and drawing 2, brittle temperature cannot rise easily. Therefore, it is possible to make [ many ] the loadings of an alumina and a boron nitride, consequently the insulating material excellent in thermal conductivity is easy to be obtained.

[0030]

[Effect of the Invention] As explained above, since the content of a high temperature conductivity bulking agent is more than 5 volume % and surface treatment of the bulking agent is carried out including the resin and the high temperature conductivity bulking agent, the high temperature conductivity insulating material of this invention is excellent in thermal conductivity also in very low temperature, and excellent in low-temperature properties, such as cold brittleness. Therefore, it is the material which can respond to the spec. to brittle temperature. Moreover, the high temperature conductivity insulating material of this invention is suitable as an insulator for insulating a superconductor. Furthermore, since an insulating material consists of a resin and a high temperature conductivity bulking agent, manufacture of a superconductivity cable is easy for it, and, moreover, long-picture-izing is possible for it. Therefore, the superconductivity cable of this invention is suitable as cables, such as the cable for very low temperature which is cooled by 100K or less very low temperature, and is used, for example, power transmission etc.

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[Translation done.]



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CLAIMS

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[Claim(s)]

[Claim 1] The high temperature conductivity insulating material which the content of a bulking agent which has high temperature conductivity is more than 5 volume %, and is characterized by carrying out surface treatment of the bulking agent including a resin and the bulking agent which has high temperature conductivity.

[Claim 2] The high temperature conductivity insulating material according to claim 1 characterized by surface treatment being processing by the silane coupling agent.

[Claim 3] The superconductivity cable which the content of the bulking agent with which it has a superconductor and an insulator, and it is the superconductivity cable by which the aforementioned superconductor is cooled with a refrigerant, and the aforementioned insulator has high temperature conductivity including a resin and the bulking agent which has high temperature conductivity is more than 5 volume %, and is characterized by carrying out surface treatment of the bulking agent.

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[Translation done.]